学校编码：10384　　分类号＿＿＿密级＿＿＿
学号：　20520071150938　　UDC ＿＿＿

厦门大学

硕　士　学　位　论　文

水滑石负载纳米金催化剂上醇类无氧脱氢反应的研究

Studies on the Oxidant-Free Dehydrogenation of Alcohols over Hydrotalcite-supported Gold Nanoparticles

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论文提交日期：2010 年 5 月

论文答辩时间：2010 年 5 月

学位授予日期：2010 年　　月

答辩委员会主席：＿＿＿＿＿＿

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2010 年 5 月

A thesis submitted to Xiamen University for M. S. Degree

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May, 2010

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摘 要

本论文针对水滑石 Hydrotalcites (HT) 负载纳米金催化剂上醇类无氧脱氢反应开展研究。研究内容主要涉及水滑石负载纳米 Au 催化剂上的醇类无氧脱氢反应和水滑石负载不同粒径的纳米 Au 催化剂的制备和表征两部分。论文通过详细考察负载 Au 催化剂的反应性能，并结合催化剂的表征结果，建立了负载 Au 催化剂上苯甲醇无氧脱氢反应的构效关联。

本论文首次发现，负载 Au 催化剂可以高效催化惰性气氛下无氢受体的醇脱氢反应，制备相应的高附加值羰基化合物与洁净能源氢气。相对于 Au 负载于不同载体的催化剂，HT 负载的纳米 Au 粒子显示出最优异的催化性能，该催化剂上苯甲醛收率大于 99%。Au/HT 催化剂的底物适用范围较广，可以高效催化带有各种取代基的苄醇、环状醇以及杂环醇的脱氢反应。Au/HT 催化剂对于饱和脂肪烃的伯醇、仲醇也有较好的催化脱氢活性。该催化剂稳定性高，可以多次循环使用。

本论文采用沉积-沉淀法制备 HT 负载纳米 Au 催化剂。通过控制制备条件，成功制备出 Au 粒径均一且在 2 nm ~ 21 nm 范围内的纳米 Au/HT 催化剂。对于相同负载量的 Au 催化剂，Au 前躯体的浓度越小、老化温度高、老化时间短等条件，有利于小尺寸的纳米 Au 粒子的生成。其中，控制 Au 前躯体浓度为 0.15 $mmol \cdot L^{-1}$，在 80 ^{o}C 下老化 1 h 时，可以制备出 Au 粒径为 2.2 nm 的 Au/HT 催化剂。

针对催化剂的构效关联的研究表明，载体表面的酸碱性和纳米 Au 粒子尺寸是决定 Au/HT 催化剂性能的关键因素。表面同时具有适量酸性位和碱性位的载体，例如 HT，是高效催化苯甲醇无氧脱氢反应的必要条件。碱性位有利于载体与醇分子形成醇盐中间体，酸性位有利于 Au-H 物种的脱除生成氢分子。Au/HT 催化的苯甲醇无氧脱氢反应是结构敏感反应，Au 粒子尺寸越小，苯甲醇的本征 TOF 越高。其中 2.1 nm 的 Au 粒子上苯甲醇的本征 TOF 可达 796 h^{-1}，是目前报道的醇无氧脱氢体系的最高值。以二十面体晶形近似计算了 Au 粒子表面不同配位状态的 Au 原子数目。我们认为随 Au 粒径减小而增加的表面低配位 Au 原子，包括棱原子和角原子，是催化苯甲醇脱氢反应的高活性物种。

关键词：醇；无氧脱氢；水滑石；Au 纳米粒子；结构敏感

Abstract

This dissertation focuses on the studies of the oxidant-free dehydrogenation of alcohols over hydrotalcite-supported gold nanoparticles. Consisted of two parts, the oxidant-free dehydrogenation of alcohols over gold nanoparticles on hydrotalcites, as well as the preparation and characterization of hydrotalcite-supported size controled gold nanoparticles has been discussed. And the correlation between the structure characters of gold catalysts and their catalytic behaviours has been also established based on the detailed characterizations.

It is the first time to demonstrate supported gold nanoparticles are highly active and selective catalysts fot the oxidant-free dehydrogenation of alcohols, giving the valuable corresponding carbonyl compounds and hydrogen. Among gold nanoparticles loaded on various supports, Au/HT exhibited the highest yield of benzaldehyde above 99%. Au/HT catalyst was efficientive for the dehydrogenation of various alcohols, including benzylic alcohols with different substituents, alicycli alcohols, heterocyclic alcohols, as well as the less active linear aliphatic alcohols although the efficiency was lower. The present Au/HT catalyst could be used repeatedly without any significant decreases in benzyl alcohol conversion and benzaldehyde selectivity.

The Au/HT catalysts were prepared by the deposition-precipitation method, especially 2 nm ~ 21 nm size-controled gold nanoparticles were successfully synthesized under different preparation conditions. For the constant gold loading samples, the diluter the gold precursor was, the higher the aging temperature was, the shorter the aging time was, the smaller gold nanoparticles were likely to get. Specificly, 2.2 nm gold nanoparticles could be synthesized at 80 ^{o}C by 0.15mmol·L^{-1} gold precursor for 1 h.

It was showed that the nature of the supports and the gold nanoparticle sizes played a key role in the gold-catalyzed dehydrogenation of benzyl alcohol. We proposed that the acid-base bifunctional supports, such as HT, were much superior to the basic or the acidic supports. The basicity of the surface was prone to abstract

proton from alcohol to yield an alkoxide intermediate, and the acidicity of the surface was reactive with hydride species to produce hydrogen molecules. It was found that the dehydrogenation of benzyl alcohol over Au/HT catalyst was a structure sensitive reaction, the TOF reached 796 h^{-1} on 2.1 nm gold nanoparticles, which was the highest for the dehydrogenation of alcohols that have been ever reported. We estimated the tendency of gold atom numbers located on the suface sites, and found that the defect (edge and corner) sites significantly increased with the decreasing of gold diameter by using icosahedron as the geometric model for gold particle, which suggested that both edge and corner gold atoms were catalytic active species in the dehydrogenation of benzyl alcohol.

Keywords: alcohol; oxidant-free dehydrogenation; hydrotalcites; gold nanoparticles; structure sensitive